STUDIES OF THE CHEMISTRY OF THE N-ARYLPYRAZOLINES

BY

FRANK VERBANAC

B.S., Wayne University, 1941
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor Harold R. Snyder for suggesting this study and for his guidance and advice during the course of the investigation.

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Introduction

Phenylhydrazones of a large variety of carbonyl compounds have been converted to substituted indoles by a number of acid catalysts (1,2). The effect of some of these reagents on N-arylpyrazolines has not been thoroughly investigated. The transformation of N-phenyl-Δ^2-pyrazoline to *bis*-N-phenyl-Δ^2-pyrazoline under the influence of hydrogen chloride has been reported, but the structure of the *bis*-pyrazoline has not been elucidated (3).

The object of the present investigation was the study of the effect of certain acid reagents on various N-phenylpyrazolines. In particular, it has been concerned with the establishment of the structure of *bis*-N-phenyl-Δ^2-pyrazoline.

Discussion Of Results

The empirical formula, $C_{18}H_{18}N_4$, has been established for *bis*-N-phenyl-Δ^2-pyrazoline. Infrared studies of the compound indicate the presence of the N-phenyl-Δ^2-pyrazoline ring system. 1-Phenylpyrazole-3-carboxylic acid and the dehydrogenated compound, $C_{18}H_{14}N_4$, have been obtained as oxidative degradation products. The latter compound was reduced to the *bis*-pyrazoline. The isolation of the compound, $C_{18}H_{14}N_4$, and the 3-carboxylic acid, together with the infrared studies, is evidence that the *bis*-pyrazoline is a bipyrazolinyl. The three position of one of the pyrazoline units must be a point of union. The possible structures are: 1,1′-diphenyl-3,4′-bipyrazolinyl, 1,1′-diphenyl-3,5′-bipyrazolinyl and 1,1′-diphenyl-3,3′-bipyrazolinyl. The degradation product, $C_{18}H_{14}N_4$, must be one of the corresponding bipyrazolyls.

1,1′-Diphenyl-3,3′-bipyrazolyl was prepared and the intermediate products, 5-methyl-1,1′-diphenyl-3,3′-bipyrazolyl, 5-

methyl-1,1′-diphenyl-3,3′-bipyrazolyl-5′-carboxylic acid and 1,1′-diphenyl-3,3′-bipyrazolyl-5,5′-dicarboxylic acid, have been characterized. The bipyrazolyl was not identical with $C_{18}H_{14}N_4$.

Ethyl 3-(5-methyl-1-phenylpyrazolyl)-acetate, an intermediate in a proposed synthesis of the 3,4′-bipyrazolyl, has been prepared. The corresponding 3-(5-methyl-1-phenylpyrazolyl)-acetic acid was also obtained.

An attempted synthesis of 3-(1-phenylpyrazolyl)-acetic acid by a lithium-hydrogen exchange of 3-methyl-1-phenylpyrazole with *n*-butyllithium, followed by carbonation, yielded 3-methyl-1-phenylpyrazole-5-carboxylic acid.

Boron trifluoride and ferric chloride caused a partial conversion of N-phenyl-Δ^2-pyrazoline to *bis*-N-phenyl-Δ^2-pyrazoline. Similarly, 1,5-diphenyl-Δ^2-pyrazoline was converted to *bis*-1,5-diphenyl-Δ^2-pyrazoline. Hydrogen chloride also transformed the latter compound to the *bis*-pyrazoline.

The action of hydrogen chloride, ferric chloride and boron trifluoride on 3,5,5-trimethyl-1-phenyl-Δ^2-pyrazoline did not produce the corresponding *bis*-pyrazoline. Boron trifluoride was without effect on 1,3,5-triphenyl-Δ^2-pyrazoline, 1,3-diphenyl-Δ^2-pyrazoline and 3-methyl-1,5-diphenyl-Δ^2-pyrazoline. It may be tentatively stated that alkyl or aryl groups in the three position of the pyrazoline nucleus of N-phenylpyrazolines prevent the formation of the corresponding *bis* compounds.

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VITA

The author was born near Zagreb, Jugoslavia, on January 20th, 1920. He came to the United States in May, 1928. He received his elementary education in the public schools of Detroit, Michigan, graduating from high school in January, 1936. In June, 1937, he entered Wayne University, from which he received the degree of Bachelor of Science in Chemistry in 1941. He was employed as a chemist by the Gelatin Products Company in Detroit, Michigan, from March, 1942, until September, 1946, at which time he entered the Graduate College of the University of Illinois. He received the degree of Master of Science in October, 1947. From September, 1946, to June, 1949, he held an Assistantship in Chemistry.

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